AN EXPERIMENT WITH HEAVY WATER

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In connection with a study of the chemistry of deuterium, we have had occasion in this laboratory to investigate the reaction of carbon dioxide on sodium carbonate dissolved in water containing 0.162% deuterium oxide. Possible reactions may be formulated as:[2]

1) $H_2O+D_2O+Na_2CO_3+CO_2 \longrightarrow NaHCO_3$ (preferentially)
2) $H_2O+D_2O+Na_2CO_3+CO_2 \longrightarrow NaDCO_3$ (preferentially)
3) $H_2O+H_2\mathbf{O}+Na_2CO_3+CO_2 \longrightarrow NaHCO_3$ (preferentially)
4) $H_2O+H_2\mathbf{O}+Na_2CO_3+CO_2 \longrightarrow NaHC\mathbf{O}_3$ (preferentially)

Equations (2) and (4) will yield a product which on thermal decomposition should give sodium carbonate, carbon dioxide, and a water of greater density than that taken for the synthesis of the bicarbonate; while a purely chance distribution of the light and heavy isotopes of hydrogen and oxygen, or a particular combination of equations (1) and (4), should result in a bicarbonate which would yield a water having the same density as that used for the synthesis.

EXPERIMENTAL

A sample of commercial "electrolytic water" containing 0.05% of deuterium oxide was further concentrated by electrolysis until its specific gravity with respect to ordinary water was 1.0001751 (at 25° C.), according to quadruplicate determinations made with two separately purified samples, and using two floats. Our float equilibrium temperatures were determined by the method of Emelius *et al.* (1)

A sample of 180 cc. of this water was saturated with anhydrous Na_2CO_3 (Merck Reagent) and placed in a closed reaction vessel agitated by rocking. Tank carbon dioxide was scrubbed with sulfuric acid, passed through glass wool, a tower of anhydrous magnesium perchlorate, and then over the sodium carbonate solution; the excess gas escaping to the atmosphere through another drying tower. Passage of the gas was continued for 48 hours. About 50 g. of $NaHCO_3$ precipitated and was separated by filtration; the precipitate was dried for 10 hours in vacuo over

[1]Contribution from the chemical laboratory of Miami University.
[2]The symbol **O** referring to the heavy isotope, O^{18}.

sulfuric acid; and then was decomposed by heating in a pyrex tube. It yielded 7.545 g. of water, weighed after purification by redistillation. As this was too small a sample for a density determination, it was mixed with 17.019 g. of ordinary water (previously thrice distilled) and the specific gravity of the mixture with respect to ordinary water was determined as 1.0000536 in duplicate determinations; the mixed sample being again redistilled between the two density measurements. Assuming that the volumes of the two water samples are additive, the density of the water recovered by decomposition of the bicarbonate must have had a specific gravity with respect to ordinary water of 1.0001829.

The filtrate from the precipitated bicarbonate was distilled from the residue remaining upon its evaporation, and twice redistilled; approximately 150 cc. was recovered after purification. Density determinations were then made upon it, using two floats; the sample was again distilled, and the density determinations were again carried out. The specific gravity with respect to ordinary water was 1.0001699.

The equilibrium temperatures for the floats used are recorded below, the temperatures being read from a Beckmann thermometer calibrated against a Centigrade thermometer certified by the Bureau of Standards.

Equilibrium temperature for Float:	No. I	No. II
Redistilled common water (Expt. 1)	24.539°	24.827°
" " " (Expt. 2)	24.538	24.828
Redistilled heavy water (Expt. 1)	25.220	25.503
" " " (Expt. 2)	25.218	25.506
Recovered filtrate water (Expt. 1)	25.198	25.481
" " " (Expt. 2)	25.198	25.490
Diluted water from $NaHCO_3$ (Expt. 1)	24.746	.....
" " " " (Expt. 2)	24.751	.....

These temperatures indicate that if the specific gravity of ordinary water is taken as unity at the equilibrium temperature, we have for:

	Specific gravity	% D_2O
Heavy water taken for the experiment	1.0001751	0.162
Heavy water recovered from filtrate	1.0001699	0.157
Heavy water recovered from bicarbonate	1.0001829	0.169

DISCUSSION

These experiments indicate that a slight concentration of deuterium or of a heavy oxygen isotope occurs in the formation of sodium bicarbonate. The probability is that **O** is concentrated, as Urey and Greiff (2) have recently shown the fractionation:

$$2\,H_2\mathbf{O} + CO_2 \longrightarrow 2\,H_2O + C\mathbf{O}_2$$

while from a consideration of the speed with which ionogen equilibria are established we should be led to expect a purely

chance distribution of $NaHCO_3$ and $NaDCO_3$ molecules; the concentration of $NaDCO_3$ being in direct ratio to the concentration of D_2O in the solution water.

REFERENCES CITED

(1) **Emelius, James, King, Pearson, Purcell, and Briscoe.** J. Chem. Soc., (1934), 1948.

(2) **Urey and Greiff.** J. Am. Chem. Soc., *57*, 321 (1935).